EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** **Ion-specific effects in colloidal gel formation**	**Experiment number:** **02-01-846**
Beamline: BM02	**Date of experiment:** from: 13 July to: 15 July	**Date of report:** 27/02/2015
Shifts: 6	**Local contact(s):** Cyril Rochas	*Received at ESRF:*

Li Zhang[1]*, Alesya Mikhailovskaia[1]*, Doru Constantin[1]*, Julien Schmitt[1]*, François Muller[2]*, Anniina Salonen[1]*, *[1]LPS, CNRS and Univ. Paris Sud, France ; [2]Nano@ECE Group, ECE Paris Ecole d'Ingénieurs.*

Report:

Attractive interactions in colloidal systems can lead to the formation of gels (1, 2). Understanding and controlling this process is crucial to numerous technologies in a diverse range of areas from food processing, pharmaceutics and ceramics. Colloidal silica is nontoxic and can be found, for instance, in construction materials, paints and food products. The system is also well characterised, which makes it an excellent choice to study the gelation process. One of the ways to induce gelation is to add salt to the dispersion of silica particles. We had observed that the timescales of gel formation are very different depending on the counterion, so the time to form a gel with equivalent concentrations of NaCl and KCl can vary by a factor of five. The aim of the proposal was to study the local structure of the gels at the end of the gel formation process and as a fucntion of time with different salt concentrations and particle volume fractions with both NaCl and KCl. We find an unexpected dependence of the structural transition time as a function of the volume fraction of particles, that is still to be fully explained. We also show that the concentration and type of salt used, only has an influence on the timescales of gel formation but not on the structure or mechanical properties of the final gel.

Samples measured and data treatment

We have measured samples with a silica concentration ϕ of 2, 4, 9, 12, 17 vol% and an added salt concentration c_s of 100, 200, 300 or 500 mM, either NaCl or KCl. Samples have been prepared 1 and 2 weeks prior to experiments to acces structure after an equilibration period, and they have also been prepared on site to access the kinetics immediately and within days of preparation.

The form factor $|F(q)|^2$ of the silica particles was calculated from the scattered intensity $I(q)$ of dilute solutions with high salt concentration (where the electrostatic interaction is screened, and the structure factor can be considered equal to 1). Its uncertainty was estimated from the difference between various individual curves. The structure factor is then obtained as $S(q) = I(q)/|F(q)|^2$.

Static Structure

We have measured the structure factors $S(q)$ of the different samples once they have stopped evolving. Figure 1 shows the structure factor $S(q)$ as a function of q for five different ϕ values, 300 mM of either NaCl (solid lines) or KCl (dashed). All samples shown form solid-like gels within a few days.

Above 0.02 $Å^{-1}$, all structure factors are very similar, indicating that the liquid order is hardly influenced by the concentration of particles or type of salt used. However, at lower q values, (over larger length scales) they become very different. The form of the $S(q)$ changes strongly with ϕ: the lower the concentration, the steeper the slope is. There is no clear dependence on salt concentration.

The low q-dependence for gelled samples can be linked to their fractal dimension, which in turn is specific for a given gel formation process. The $S(q)$ of the samples with $\phi = 2$ and 4 vol% decay as $q^{-2.1}$, a

value typical for a gel formed by reaction limited aggregation (3, 4), showing that, even at the highest c_s (500 mM) and for both types of salt, the electrostatic repulsion between the particles remains important.

Increasing the packing fraction leads to a change in the structure factors, which deviate strongly from the $q^{-2.1}$ behaviour. The fractal nature of the aggregates is reduced, as the q dependence becomes increasingly flat. This is in agreement with what has been observed in particle and lattice simulations (5).

For the salt specific effects, we can note that with a fixed c_s = 300 mM the counterion type seems to have more influence on the structure as ϕ increases, however this is the case only with the data set shown. It is true for all the data that the variation in the low q behaviour from one salt concentration to another is more important at higher ϕ_{TMA}. This means that all the graphs at 2 or 4 vol% are almost identical (for all c_s), while they show important, but random, variation at 12 and 16 vol%.

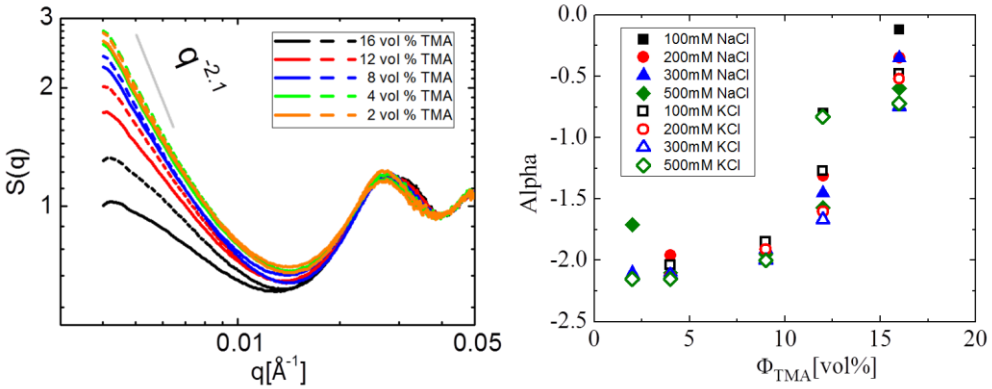

Figure 1: Structure factor S(q) changed with q at different volume fraction of TMA (Φ=2%-16%), 300mM salt, NaCl with solid line and KCl with dashed line. (b) α changed with the volume fraction of TMA at all salt concentrations(100-500mM).

Kinetics

The kinetics at the local scale is followed with the measurements of the $S(q)$ in time. We can see the evolution of the $S(q)$ after sample preparation in Figure 2(a) for a sample with ϕ = 12 vol% and c_s = 200 mM NaCl. At short times the $S(q)$ is typical for a fluid sample. With time, the low-q structure factor increases indicating structuration at larger length-scales, and can indicate the formation of a gel.

In order to quantify the time scales of change, we characterized the evolution of the samples by plotting the structure factor at a fixed scattering vector (q_0=0.005 Å^{-1}) as a function of sample age: $S(q_0, t)$. The evolution of $S(q_0)$ is shown in Figure 2(b). From such curves we extract the inflection point of the curve defined as τ_X, which is used as an estimate of the transition time. Therefore τ_X is the characteristic time linked to the arrest of the structural evolution at q = 0.005 Å^{-1} (corresponding to 1256 Å, about 5 particle diameters).

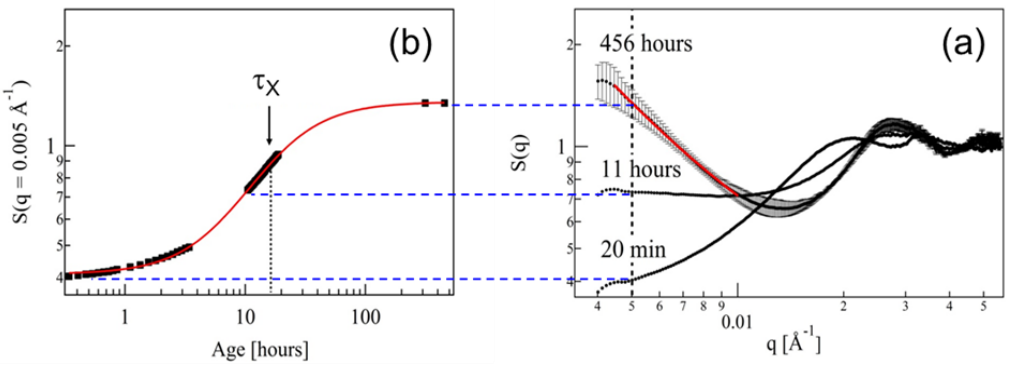

Figure 2: (a) S(q) for a sample with 12 vol% TMA, 200 mM NaCl, at three times after preparation. For clarity, error bars are only shown for one curve. The solid red line is a power-law fit (see text). (b) Time evolution of the structure factor S (q=0.005 Å^{-1}) for the same sample (dots) and fit with a sigmoidal function. The estimated transition time τ_X (16.26 hours) is indicated.

We have measured the τ_X for all the sample and plotted it for both salts in Figure 3. These have been compared to gelification times measured by macroscopic sample observation. The macroscopic time is theoretically expected to evolve with ϕ with a power law of -1.7 and is experimentally found to do so.

If we estimate the time it takes for the structure to stop evolving and compare it with the gel formation time we can see that for most of the samples the gel becomes stress-bearing much before the structure has been fixed at the scale of a few colloidal particles.

Interestingly, the τ_X decrease more weakly with ϕ than the macroscopic times and at no point could we describe it using a power law of -1.7. Of course there is no reason why a local structural transition should evolve in the same way as the macroscopic yield stress. At the moment we do not know what could be at the origin of the weaker ϕ variation of the τ_X. An article based on these results has been submitted (6).

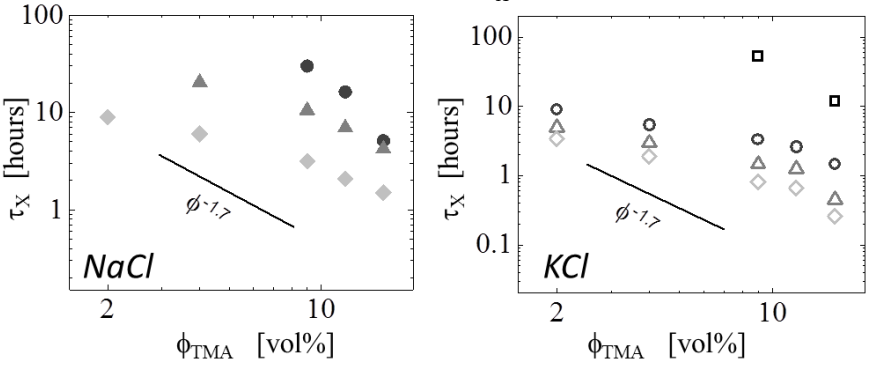

Figure 3: Transition times obtained from SAXS measurements (τX) at different TMA volume fractions and salt concentrations. 100mM NaCl(squares), 200mM NaCl(circles), 300mM NaCl(triangles), 500mM NaCl(diamonds). Filled symbols correspond to NaCl and empty ones to KCl.

1. Zaccarelli E. Colloidal gels: equilibrium and non-equilibrium routes. J Phys-Condes Matter. 2007;19(32).
2. Guo H, Ramakrishnan S, Harden JL, Leheny RL. Gel formation and aging in weakly attractive nanocolloid suspensions at intermediate concentrations. J Chem Phys. 2011;135(15).
3. Schaefer DW, Martin JE, Wiltzius P, Cannell DS. FRACTAL GEOMETRY OF COLLOIDAL AGGREGATES. Physical Review Letters. 1984;52(26):2371-4.
4. Ferri F, Frisken BJ, Cannell DS. STRUCTURE OF SILICA-GELS. Physical Review Letters. 1991;67(25):3626-9.
5. Rottereau M, Gimel JC, Nicolai T, Durand D. Monte Carlo simulation of particle aggregation and gelation: I. Growth, structure and size distribution of the clusters. European Physical Journal E. 2004;15(2):133-40.
6. Zhang L, Mikhailovskaia A, Constantin D, Foffi G, Tavacoli JW, Schmitt J, et al. Speeding up of colloidal gel formation by changing the counterion. 2015.